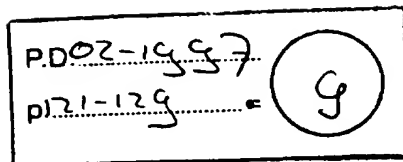




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Synthesis of phosphate-silicate apatites at atmospheric pressure

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Abstract

Natural silicate-containing apatites (called britholites) are found in rare geological areas and contain large amounts of actinide and lanthanide elements [1-3]. Such compounds can be synthesised by a solid state reaction at high temperatures. As for the well-known fluoroapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ and oxyapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{O}\square$ (\square = vacancy) these compounds were prepared by the substitution pair $(\text{La}^{3+}, \text{SiO}_4^{4-})$ for $(\text{Ca}^{2+}, \text{PO}_4^{3-})$. The general formula of the compounds are given by $\text{Ca}_{10-x}\text{La}_x(\text{SiO}_4)_x(\text{PO}_4)_{6-x}\text{F}_2$, $0 \leq x \leq 6$, and $\text{Ca}_{10-x}\text{La}_x(\text{SiO}_4)_x(\text{PO}_4)_{6-x}\text{O}\square$, $0 \leq x \leq 6$. They were analysed by X-ray diffraction and infrared spectroscopy. The synthesis has to be performed accurately to avoid the formation of poorly reactive intermediate phases.

Keywords: Apatite; Silicate-apatite; Britholite

1. Introduction

Apatites form a large family of isomorphous compounds with the general chemical formula $\text{Me}_{10}(\text{XO}_4)_6\text{Y}_2$, where Me generally represents a divalent cation (Ca^{2+} , Sr^{2+} , Pb^{2+} , Cd^{2+} , etc), XO_4 a trivalent anionic group (PO_4^{3-} , VO_4^{3-} , AsO_4^{3-} , etc) and Y a monovalent anion. A well-known representative member of the apatitic family is calcium phosphate fluoroapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$.

Apatites generally crystallize in the hexagonal system (spatial group P63/m) [4]; the quasi-compact arrangement of the anion groups (XO_4) forms the skeleton of the apatite and exhibits two types of channels. The first is occupied by four Me cations with a Ch symmetry, placed on the ternary axis and

called MeI. The second is occupied, on its periphery, by six Me cations with Cs site symmetry and is called MeII. The MeII cations are placed on two equilateral triangles at level 1/4 and 3/4 centered on the 6-fold axis (Fig. 1). Y^- anions are located on this axis and benefit from a large mobility.

All the elements of the apatite structure can be substituted. When the substitution concerns elements with different ionic charges it is possible to equilibrate the charge balance [5]. For example it is possible to substitute trivalent cation for divalent calcium, if the charge is balanced by substitution of a tetravalent group for the trivalent phosphate group [6-8].

Complete series of fluoro- and oxy-apatite were prepared by the substitution pair $(\text{La}^{3+}, \text{SiO}_4^{4-})$ for $(\text{Ca}^{2+}, \text{PO}_4^{3-})$. Trivalent lanthanides are considered as chemical analogues of radioactive elements, such as americium and curium, and lanthanum has been used for the synthesis. The final material are synthetic

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compounds in the initial mixture, can induce the formation of poorly reactive intermediate phases.

The two reactions of formation of the fluoro- and oxy-apatite can be represented by

$$\begin{aligned} &x/2 \text{ La}_2\text{O}_3 + 1 \text{ CaF}_2 + 3 \text{ CaCO}_3 \\ &+ x \text{ SiO}_2 + (6-x)/2 \text{ Ca}_2\text{P}_2\text{O}_7 \\ &\rightarrow \text{Ca}_{10-x} \text{La}_x (\text{SiO}_4)_x (\text{PO}_4)_{6-x} \text{F}_2 + 4 \text{ CO}_2 \end{aligned}$$

with $x = 1, 2, 3, 4, 5, 6$; and

$$x/2 \text{ La}_2\text{O}_3 + 4\text{CaCO}_3 + x/4 \text{ SiO}_2 + (6-x)/2 \text{ Ca}_2\text{P}_2\text{O}_7 \rightarrow \text{Ca}_{10-x} \text{La}_x (\text{SiO}_4)_4 (\text{PO}_4)_{6-x} \text{O} + 4\text{CO}_2$$

with $x=2, 4, 6$. In fact, for the preparation of the fluoroapatite, in order to increase the rate of the reaction and to compensate for volatilization losses, the CaF_2 quantities are multiplied by the factor 1.2 with respect to the stoichiometry.

The method consists in a preliminary treatment followed by one or several grinding-calcination cycles.

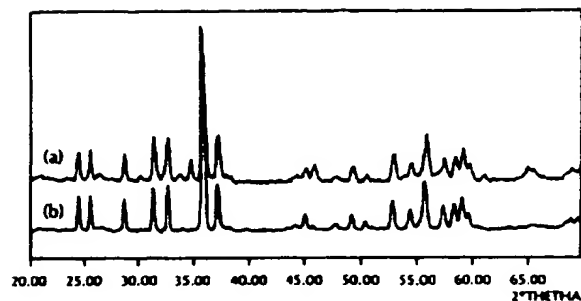


Fig. 2. X-ray diffraction diagrams of the compound $\text{Ca}_8\text{La}_4(\text{SiO}_4)_2(\text{PO}_4)_2\text{O}\square$ with one (a) and three (b) grinding-calcination cycles.

2.2.1. The preliminary treatment

A preliminary treatment is necessary to obtain well-crystallized apatites. It consists of heat treating the mixture at 900°C for several hours with intermediate grinding and allows release of CO_2 gas, giving a homogeneous mixture.

2.2.2. The grinding-calcination cycles

According to the silicate/phosphate ratio of the final apatite, the calcination temperature differs; it increases with the amount of silicate.

In the case of pure phosphate or silicate apatites, just one grinding-calcination cycle is sufficient to obtain well crystallized apatite. Apatites which contain the two anionic groups, simultaneously, need two or more treatments (Fig. 2). According to the silicate and phosphate content, three parameters have to be taken into account: the number, the temperature and the duration of the treatments.

The X-ray diffraction patterns have been obtained from powdered samples using a CPS 120 INEL diffractometer ($\text{K}\alpha_1$, cobalt, internal standard: $\alpha\text{-Al}_2\text{O}_3$) and infrared spectra have been recorded between 4000 cm^{-1} and 400 cm^{-1} using a Perkin-Elmer 7700 FTIR spectrometer.

3. Characterization

X-ray diffraction confirms that all the compounds are formed by a pure apatitic phase which crystallizes in the hexagonal system (space group: $\text{P6}_3/$

Table 1

Cell parameters and density of oxy- and fluoroapatites

Compounds	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	ρ
$\text{Ca}_8\text{La}_4(\text{SiO}_4)_2\text{F}_2$	9.6503	7.1412	575.95	4.568
$\text{Ca}_8\text{La}_4(\text{SiO}_4)_2(\text{PO}_4)_2\text{F}_2$	9.5911	7.0717	563.37	4.104
$\text{Ca}_8\text{La}_4(\text{SiO}_4)_2(\text{PO}_4)_2\text{F}_2$	9.5027	6.9806	545.90	3.652
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	9.3842	6.8878	527.71	3.174
$\text{Ca}_8\text{La}_4(\text{SiO}_4)_2\text{O}\square$	9.6351	7.1341	573.56	4.523
$\text{Ca}_8\text{La}_4(\text{SiO}_4)_2(\text{PO}_4)_2\text{O}\square$	9.5843	7.0444	561.99	4.049
$\text{Ca}_8\text{La}_4(\text{SiO}_4)_2(\text{PO}_4)_2\text{O}\square$	9.4802	6.9570	541.49	3.614
$\text{Ca}_{10}(\text{PO}_4)_6\text{O}\square$	9.4116*	6.8747*	527.74*	3.104*

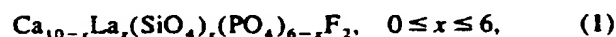
* Extrapolated values.

m). The cell parameter values are reported in Table 1.

The formation of the compound can be considered as a coupled substitution of (La^{3+} , SiO_4^{4-}) for (Ca^{2+} , PO_4^{3-}). This replacement modifies the cell parameters which increase with the simultaneous introduction of lanthanum and silicate ions.

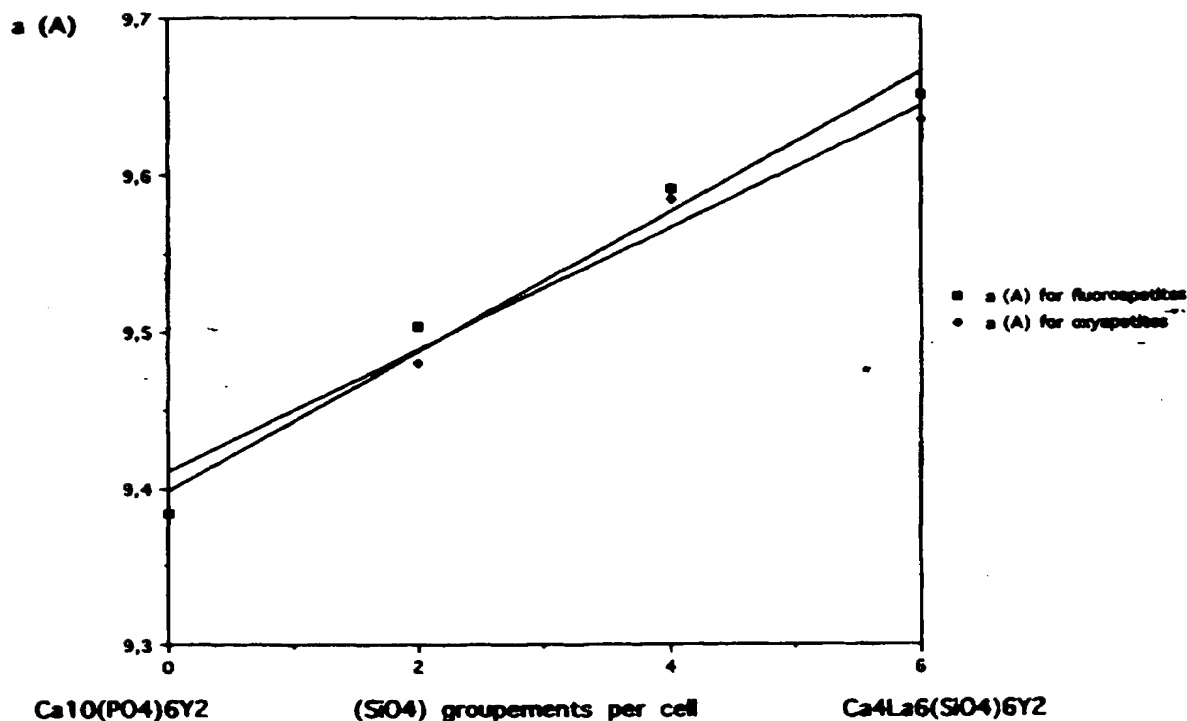
Concerning the silicate and phosphate groups, the average lengths of the Si–O and P–O bonds are respectively 1.62 Å and 1.51 Å; concerning the lanthanum and calcium cations, La^{3+} (1.03 Å) is slightly bigger than Ca^{2+} (0.99 Å). The coupled substitution induces an average radius increase of both cationic and anionic groups and, consequently, in agreement with the well-known rules of substitution in the apatitic lattice, an increase of both *a* and *c* parameters.

Figs. 3–5 plot the variations of *a* and *c* parameters and the variations of the volume of the apatite versus the amount of lanthanum (or silicate) in the cell. The linear variation is in agreement with Vegard's law and it can be concluded that oxy- and fluoro calcium-lanthanum silicate-phosphate apatites form a solid solution with the general formula



Two facts can be pointed out:

For a given lanthanum and silicate composition (same *x* value), a difference appears between oxy- and fluoroapatite parameters; this difference is quite complex to explain, and partly due to the presence of

unit cell parameters (*a*) of apatite versus silicate contentFig. 3. Variations of *a* parameters of the apatite versus the amount of silicate in the cell.

vacancies in the oxyapatite and fluorine ions inside the channels.

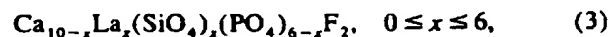
Another point concerns the calcium phosphate oxyapatite. It is impossible to obtain this compound with only O²⁻ ions in the channel. Slight hydroxylation always occurs. Nevertheless, using the regression line, the parameters of the pure oxy-apatite can be evaluated; the values: $a = 9.412 \text{ \AA}$ and $c = 6.875 \text{ \AA}$ are quite close to the values reported in the literature ($a = 9.420 \text{ \AA}$; $c = 6.890 \text{ \AA}$).

Interpretation of the IR spectra is complex. The different types of bands were assigned by comparison with the well-known fluoroapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$). The tetrahedral SiO_4 and PO_4 groups present similar vibrations. This assignment was confirmed with the variations of the intensities

and the displacement of the band correlated with the silicate and phosphate content of the apatites (Fig. 6). The data are reported in Table 2.

4. Discussion

The total substitution of SiO_4 for PO_4 in the apatitic lattice appears to be possible; the charge is balanced by the introduction of trivalent lanthanum for divalent calcium. The X-ray diffraction confirms that a solid solution exists between the two limit compounds



unit cell parameters (c) of apatite versus silicate content

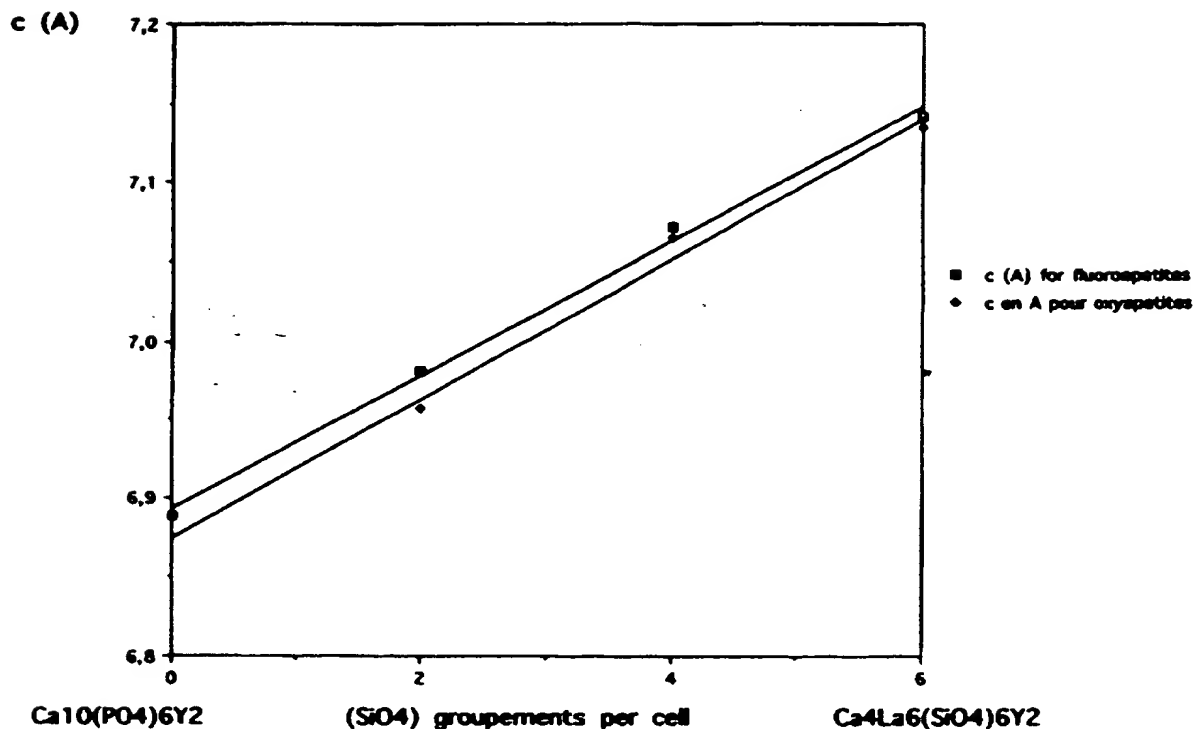


Fig. 4. Variations of c parameters of apatite versus the amount of silicate in the cell.



This solid solution follows Vegard's law.

The synthesis temperature is different for phosphate apatites and silicate apatites. Both the kinetic and the thermodynamic of the reaction would control the synthesis of such compounds.

In both cases of pure phosphate apatites and pure silicate apatites, an increase of temperature favors the reaction rate. In the case of silicate apatites, a high synthesis temperature (1400°C) is necessary to obtain a sufficient reaction rate and a pure apatitic phase. On the contrary, in the case of phosphate apatites so high a temperature can induce the formation of poorly reactive intermediate phases as for example tetracalcium phosphate $\text{Ca}_4\text{P}_2\text{O}_9$ at 1400°C

and consequently the final compound is not pure. In general these phases are poorly reactive. It is therefore difficult to obtain pure apatite, even with additional low-temperature treatments. Consequently, the synthesis of pure phosphate apatites can be more easily realized by a calcination at 1200°C.

For the intermediate compounds, a necessary compromise has to be found between the temperature and the duration of the heating. For compounds which have a high phosphate content ($x=1, 2, 3$), it is better to maintain the temperature at 1200–1250°C to increase the reaction time. If the final compound contains extra silicate phases, the temperature has to be very slowly increased. For compounds which mainly contain silicate ($x=4, 5, 6$) it is preferable to heat at high temperature for a short time.

cell volume variations of apatite versus silicate content

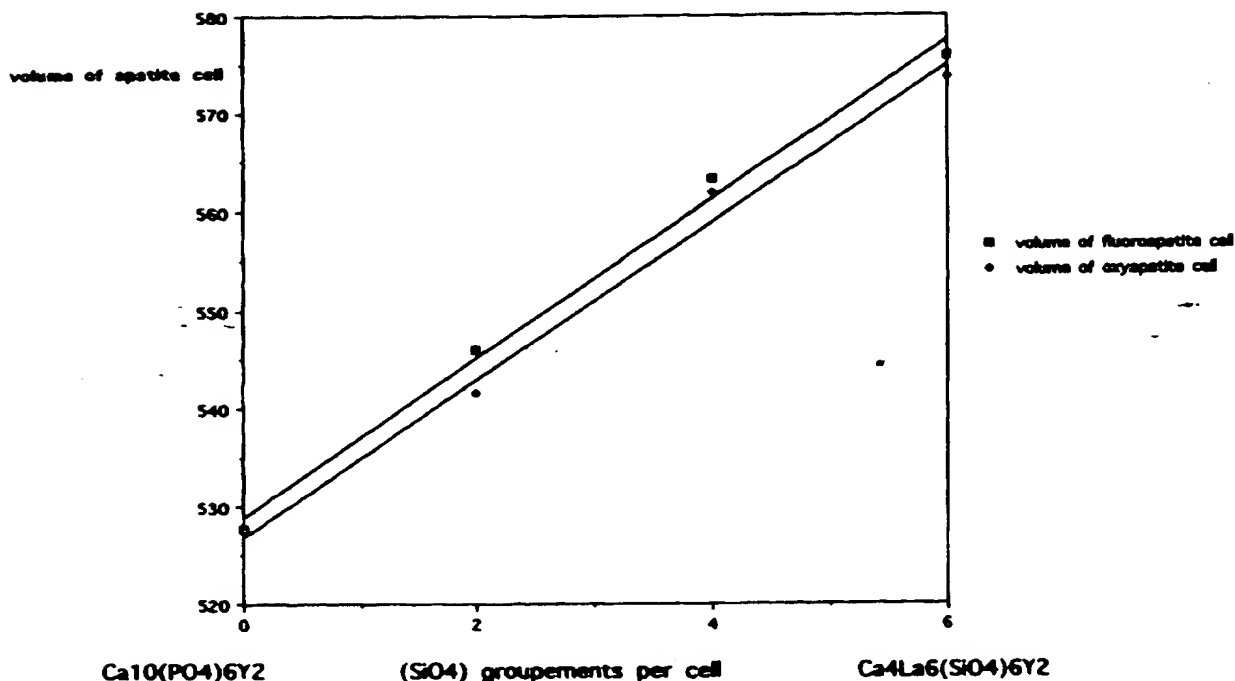


Fig. 5. Cell volume variations of apatite versus the amount of silicate.

The britholites obtained have been observed in scanning electron microscopy (Figs. 7 and 8).

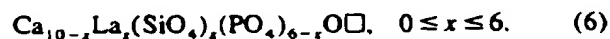
At a macroscopic level, it is interesting to notice that the total volume of the compound obtained after the first calcination decreases when the silicate content increases. This volume decrease can be correlated with an increase of the cohesion of the compound obtained. The explanation for these observations could be: at the temperature of calcination, necessary for the synthesis of silicate-phosphate apatites, $\text{Ca}_2\text{P}_2\text{O}_7$ is fused; this liquid phase favors the displacement of particles, the atomic mobility and finally contributes to increase the reactivity and to reduce the porosity.

An increase of the $\text{Ca}_2\text{P}_2\text{O}_7$ content in the initial mixture, thus would explain the decrease of volume and the increase of the cohesion of the compound obtained after the step calcination. As soon as, $\text{Ca}_2\text{P}_2\text{O}_7$ has completely reacted (consummation of the all amorphous silica phase), the formation of a

dense hard product is no more possible, even with a new step of grinding-calcination. The compound obtained is a stoichiometric silicate phosphate apatite.

5. Conclusions

It is possible to prepare apatite containing both trivalent phosphate and tetravalent silicate groups. The charge is balanced by the cationic substitution of trivalent lanthanum for divalent calcium. The general formula of such fluoride or oxygenated compounds are:



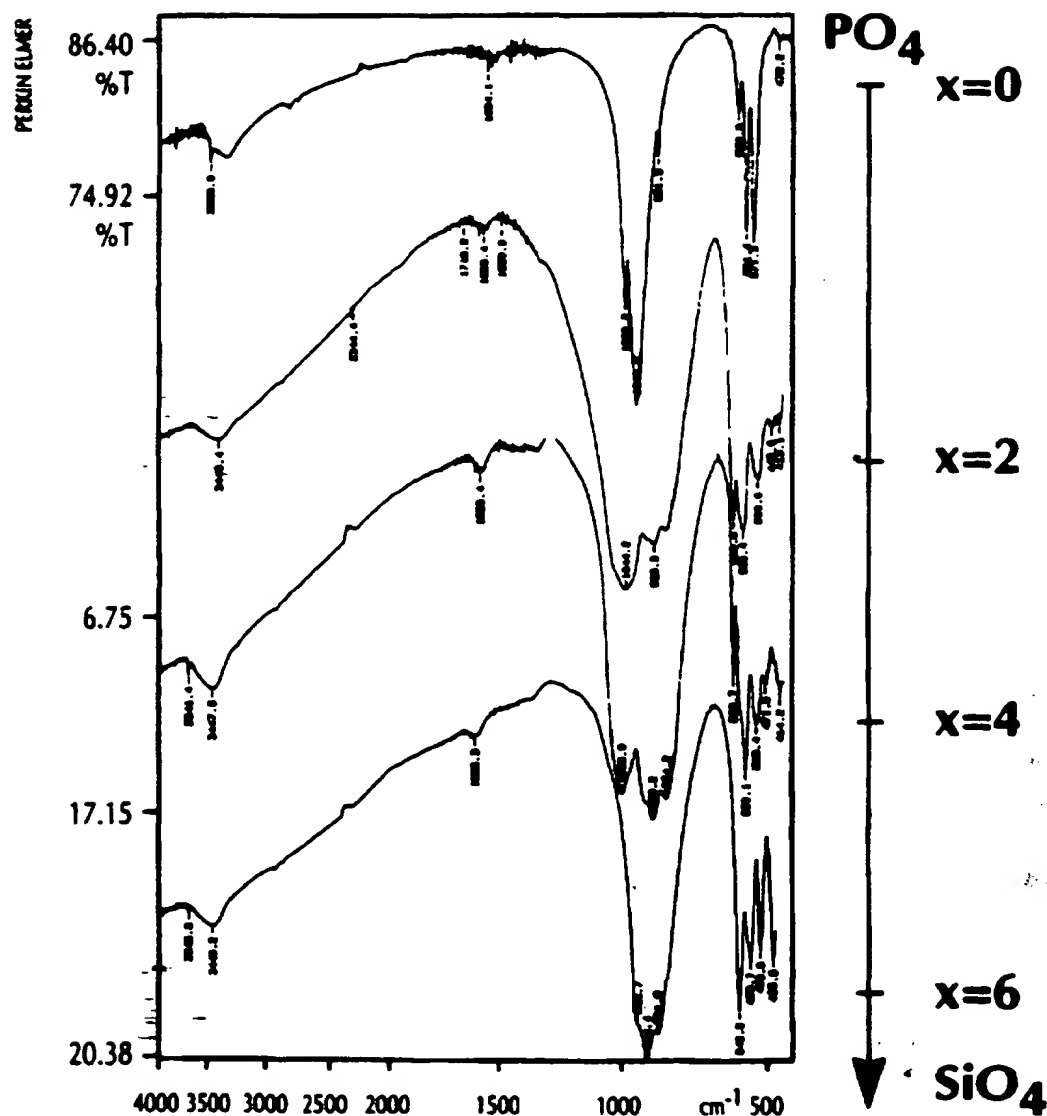


Fig. 6. Infrared spectra of the compounds $\text{Ca}_{10-x}\text{La}_x(\text{SiO}_4)_x(\text{PO}_4)_{6-x}\text{O}$ with $x = 0, 2, 4, 6$.

Calcination temperature is a very important parameter for the synthesis of apatites: it increases with the silicate content from 1200°C to 1400°C.

Lanthanum was chosen to represent the rare earth family. However, the introduction of other trivalent elements from this family can be performed in the same way.

These materials can be considered as synthetic analogues of natural apatites. According to the properties of natural silicate-apatites, the possibility of obtaining synthetic apatites with a definite composition allows the preparation of materials suitable for use as high performance matrices for long-lived radioactive wastes.

Table 2
IR absorption bands of oxy- and fluoro-apatites

	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_3 (cm ⁻¹)	ν_4 (cm ⁻¹)
IR bands of the PO ₄ in the following compounds				
Ca ₄ La ₆ (SiO ₄) ₆ F ₂	—	—	—	—
Ca ₈ La ₄ (SiO ₄) ₄ (PO ₄) ₂ F ₂	—	—	1056	574–601
Ca ₈ La ₂ (SiO ₄) ₂ (PO ₄) ₄ F ₂	954	—	1048 + sh ^a	575–602
Ca ₁₀ (PO ₄) ₆ F ₂	964	471	1045–1094	575–603
Ca ₄ La ₆ (SiO ₄) ₆ O□	—	—	—	—
Ca ₈ La ₄ (SiO ₄) ₄ (PO ₄) ₂ O□	—	—	1054	560–600
Ca ₈ La ₂ (SiO ₄) ₂ (PO ₄) ₄ O□	955	—	1044–1086	561–601
Ca ₁₀ (PO ₄) ₆ O□	962	473	1044–1090	571–601
IR bands of the SiO ₄ in the following compounds				
Ca ₄ La ₆ (SiO ₄) ₆ F ₂	884	406–459	924–962	500–542
Ca ₈ La ₄ (SiO ₄) ₄ (PO ₄) ₂ F ₂	882	414–472	932–962	514–550
Ca ₈ La ₂ (SiO ₄) ₂ (PO ₄) ₄ F ₂	886	422	932	562
Ca ₁₀ (PO ₄) ₆ F ₂	—	—	—	—
Ca ₄ La ₆ (SiO ₄) ₆ O□	882	408–459	924–963	499–542
Ca ₈ La ₄ (SiO ₄) ₄ (PO ₄) ₂ O□	882	414–472	928–953	508–550
Ca ₈ La ₂ (SiO ₄) ₂ (PO ₄) ₄ O□	887	413	928	510
Ca ₁₀ (PO ₄) ₆ O□	—	—	—	—

^a Shoulder.

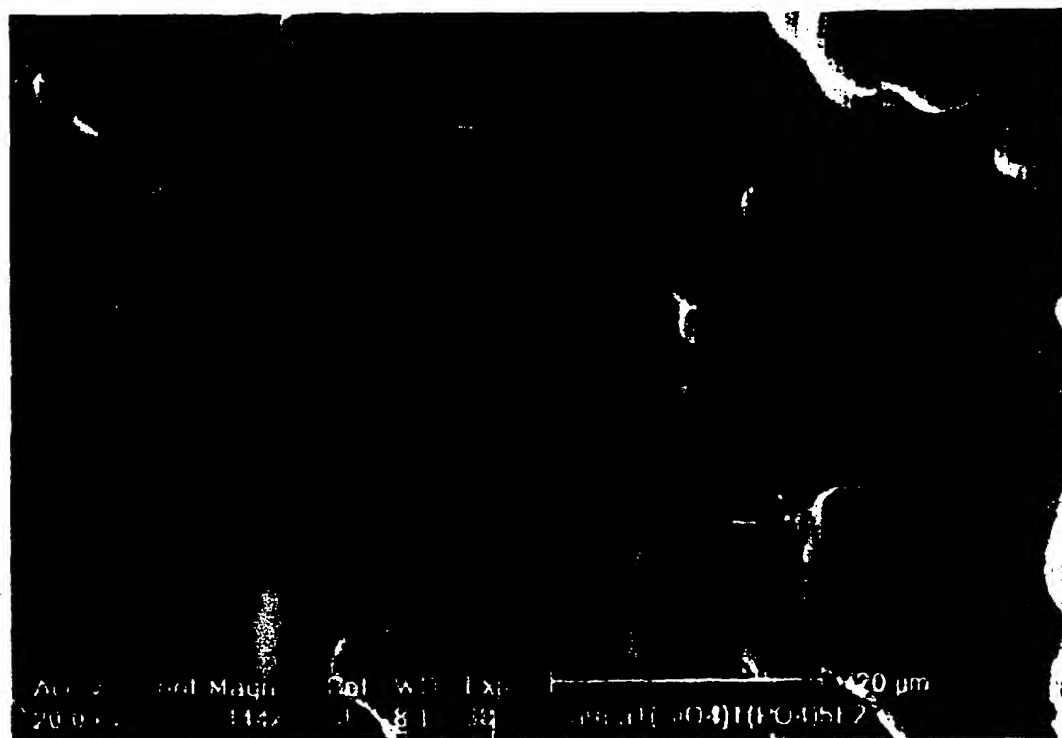


Fig. 7. Scanning electron microscopy study of britholite Ca_{10-x}La_x(SiO₄)₆(PO₄)_{4-x}F₂ with x = 1.



Fig. 8. Scanning electron microscopy study of britholite $\text{Ca}_{10-x}\text{La}_x(\text{SiO}_4)_6(\text{PO}_4)_2\text{F}_2$ with $x=6$.

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